

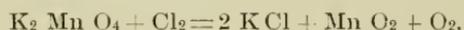
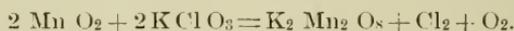
## INVESTIGATION OF THE ACTION BETWEEN MANGANESE DIOXIDE AND POTASSIUM CHLORATE IN THE PRODUCTION OF OXYGEN.

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The method for preparing oxygen by heating mixtures of potassium chlorate and manganese dioxide has been used by chemists for some time. Since, however, the manganese dioxide comes out unchanged at the end of the process, yet considerably lowers the temperature necessary for decomposition of potassium chlorate, its exact function has been and is yet imperfectly understood.

There is not only a practical, but also a very interesting theoretical question involved in the explanation of the reaction taking place in this process, and it was the desire for obtaining further light on certain points that led Professor Ransom and the writer, at the suggestion of the former, to jointly undertake a study of the facts. Some questions, the settlement of which was to be attempted, were: 1. Does variation in proportion of potassium chlorate and manganese dioxide affect the temperature at which oxygen is evolved, and, if so, what mixture yields it at the lowest temperature? 2. Is the action continuous when the mixture is heated for a long period at or just above the decomposition temperature, and what are the products? 3. Heating for a period just below this temperature, are any intermediate products formed and what are they? 4. To notice any new facts brought out by the experimental work.

Search of the literature shows that the men who have performed the most important work upon this particular phase of the subject are McLeod, Brunck and Sodeau. McLeod had noticed the well-known fact that a gas resembling chlorine was evolved with oxygen, and in 1889, published a statement of experimental work, deducing the following reactions:



Upon this basis he explained the supposed fact that free chlorine is evolved only at the beginning of the process, since chlorine is liberated by the first reaction and at the lowest temperature, and that corresponding to this free chlorine, there was a certain amount of undecomposed potassium manganate at the end. In 1893 Brunck argued that if these reactions

took place, the residue should either be alkaline or contain potassium manganate, or permanganate, and that he could obtain no evidence that either was the case. He brought forward experimental evidence to prove that the evolved gases did not contain more than a mere trace of chlorine and affirmed his belief that the odor and the property of bluing starch and potassium iodide paper was due to ozone. In 1894 McLeod stated that when the gases were led through alkaline silver nitrate solution, and this later acidified, a precipitate was obtained which corresponded in quantity with the alkalinity of the residue in the generator. He could obtain no evidence of ozone. Some further work was done by these men but they did not apparently succeed in settling the point at issue.

Sodeau, in 1901, proved that the action of manganese dioxide, barium sulphate, sand, and other supposedly inert bodies increased the evolution of oxygen not mechanically, but chemically.

#### EXPERIMENTAL.

The apparatus used in the experimental part of the present investigation was very simple. Hard glass test-tubes five inches in length, with side necks, were used for heating the mixtures, these being placed in a bath of Wood's fusible metal, heated in a thick cast-iron cup large enough to accommodate five tubes. A thermometer was also placed in the metal. Short delivery tubes, with ends drawn to a narrow aperture, led to a vessel for collecting the evolved gases in test-tubes over water.

The manganese dioxide used was Merck's "Artificial Pure," and previous to using was heated for several hours in an open dish over a free flame, in order to remove moisture; it was then placed in a glass stoppered bottle for keeping. Eimer and Amend's potassium chlorate was dried for six hours at 105°-110° for this purpose. It was not labeled "C. P." but tested free from chlorides both before and after drying.

The first mixtures were made in the following molecular ratios of manganese dioxide to potassium chlorate: 10:1, 2:1, 1:1, 1:2, 1:10. These were ground together, placed in the tubes, and slowly heated. At 150°-165° a gas was evolved from all, showing the presence of oxygen by means of a glowing spark, and giving a strong odor of chlorine or chlorine oxide. This odor is certainly not that of ozone and may be either chlorine or chlorine oxide, or both. In this paper it will be provisionally called chlorine. It was noticed that considerable moisture collected upon the

upper parts of the generator tubes, indicating that at least one of the substances still contained moisture.

Other portions of the same mixtures as above were dried in their tubes for several hours at  $100^{\circ}$ - $105^{\circ}$ . Chlorine was evolved upon heating to  $122^{\circ}$  but no oxygen was evidenced by a spark. At  $135^{\circ}$  the rate of evolution of oxygen was approximately in direct proportion to the amount of manganese dioxide used, this being the reverse of the case when the materials were not dried. This, however, is not stated as a definite law.

Four other mixtures were more carefully dried, then heated in the bath. Chlorine was evolved at  $140^{\circ}$ , oxygen at  $168^{\circ}$ .

It was early seen that no reliable results could be obtained so long as the manganese dioxide held moisture. To determine whether this substance was hygroscopic, and if so, roughly the amount of water taken up, some freshly dried material was weighed in a closed bottle, then allowed to stand open for definite periods, weighing after each period. In twenty minutes its weight increased approximately 1 per cent.; after one and a half hours, 3 per cent.; after forty-five hours, 6 per cent.

To determine the difference in behavior due to this moisture, two mixtures were prepared: In (X) the manganese dioxide was dried over a free flame, weighed in a glass-stoppered bottle and the weighed potassium chlorate added. The other mixture (Y) was of potassium chlorate and ordinary undried manganese dioxide; both were molecular mixtures. In this and future experiments chlorine was tested for by starch and potassium iodide paper. At  $125^{\circ}$  (X) gave no chlorine or oxygen, (Y) gave large quantities of chlorine but no oxygen. Much moisture collected in (Y). At  $148^{\circ}$  a steady stream of oxygen came from (Y), continuing as long as heated. No trace of chlorine or oxygen came from (X).

More manganese dioxide was purified by digesting in cold distilled water, then washing until free from chlorides. The wash water contained small amounts of manganese and calcium. The washed mass was dried for two and a half hours at  $200^{\circ}$ - $210^{\circ}$ .

Four tubes were now filled with mixtures in molecular proportions, transferring the manganese dioxide quickly at  $200^{\circ}$  to the hot weighing bottle, cooling, weighing, adding the ground and weighed potassium chlorate, and mixing. The mixtures were quickly transferred to the tubes, the delivery tubes of which were in this case guarded with granular calcium chloride. A tube of dry potassium chlorate was heated with the others, in order to judge the amount of expanding air forced over.

The tubes were kept at 135°-140° for four and a half hours; no gas was over beyond that due to simple expansion, and not the slightest trace of either chlorine or ozone was found in any generator tube. No oxygen could be discovered. The mixtures upon testing were found to contain a considerable amount of chlorides. The temperature was raised to and kept at 150° for three hours and no chlorine or oxygen was produced. The quantity of chlorides seemed to be increased. At 173° all of the tubes began to evolve oxygen and so long as this temperature was maintained a steady but slow stream of oxygen was produced. No trace of chlorine, chlorine oxide or ozone was produced as high as 180°.

At this point the work was stopped for lack of time. Thus far a few conclusions may be provisionally advanced:

The conditions under which oxygen is ordinarily produced are not ideal, and the moisture always present materially influences the reactions. This moisture makes possible the production of oxygen at a lower temperature than in the case of dry materials, also the formation of chlorine or chlorine oxide, or both, as low as 125° and before oxygen is evolved. This may be due to hydrolysis of the potassium chlorate or chloride, thus allowing oxidation by the manganese dioxide. It is possible and even probable that no chlorine would be evolved at any temperature within the ordinary range of heating, if the materials were entirely free from moisture. In such a case, McLeod's explanation must fail, since if it be true, the formation of free chlorine is a necessary step in the evolution of oxygen.

This point, with others mentioned, will be more fully investigated by future work, and it is hoped that some facts of interest may be brought out during the investigation.

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## ACTION OF HEAT ON MIXTURES OF MANGANESE DIOXIDE WITH POTASSIUM NITRATE AND WITH POTASSIUM BICHROMATE.

J. H. RANSOM.

The fact that different metallic oxides mixed with potassium chlorate cause the latter to evolve oxygen at considerably lower temperatures than when heated alone has long been known, though the nature of the chemical action involved is not with certainty established. No work has been done, so far as I am aware, to see what the effect of these oxides might be on other substances decomposable by heat.